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Appleton, Wisconsin

MOLECULAR STRUCTURES OF LIGNOSULFONATES MECHANICAL AND ADHESIONAL BEHAVIOR

Project 2421

Report Fifteen

A Progress Report

to

ENVIRONMENTAL RESEARCH GROUP

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SUMMARY

The focus of Project 2421 has been on the adhesional and mechanical behavior of lignosulfonate adhesives, and their relationship to adhesive bonding strength, particularly in plywood operations. These behavioral properties were found to be similar to good plywood adhesives and they thus have good potential. The low cohesive strength has been found to be a major limitation in lignosulfonate adhesives and this can be improved by implementing cross-linking reactions. The time, temperature, and concentration conditions for the cross-linking reaction of lignosulfonates with Catalin CR-9357 (a phenol-formaldehyde resin) were surveyed systematically with the goal of optimizing this reasonably successful plywood adhesive (i.e., the Holderby formulation). In this report, the failure of the lignosulfonates to achieve acceptable plywood bonding is shown to be due (1) to low reactivity under boiling limited temperatures existing during curing time, and (2) to degradation of wood at the adhesive interface from the high acid conditions of the adhesive. It is then shown that under neutral or alkaline conditions the reactivity of calcium spent sulfite liquor (CaSSL) with phenol-formaldehyde resins or their components is low. And finally, pretreatment of the CaSSL with paraformaldehyde or resorcinol was shown to significantly improve the reactivity at these higher pH's with measurable improvement in plywood bonding found. The report concludes with a summary of the project and a suggested future program to optimize plywood bonding with CaSSL adhesives at high pH.

An iron-constantan thermocouple system was set up to record the temperature of the adhesive during the curing time. The disk method used to determine

cross-linking reactivity employed two wood veneers which promoted a very rapid rise in temperature, reaching the platen temperature in 4 to 6 min. The plywood operation (two 3-ply layups per press) involved six wood veneers which promoted a rapid temperature rise to about the boiling point of the adhesive followed by a time of only slowly increasing temperature which continues, in most cases, until the maximum time of press, 6 min. In this case, the temperature profiles do not change much with platen temperature within the range studied (275 to 345°F.). The temperature profiles of the inner and outer glue lines differed significantly from each other, although they were both low compared to the profiles from the disk method. However, the plywood bonding strengths of these glue lines were not significantly different from each other.

A lignosulfonate-Catalin adhesive, which had good water insolubility when cured by the disk method but gave poor plywood bonding, was cured in a 2-ply, disk method arrangement, and then backed by a third veneer bonded with a room temperature cured, waterproof glue. This plywood gave dry tensile and boil test results equivalent to those from plywood bonded with the Holderby formulation. This supports the relationship between water insolubility measurements and plywood bonding strength, and it indicates that these adhesives are quite sensitive to the true curing temperature. This finding coupled with the above temperature-time data indicates that, in the plywood operation, the ultimate bonding success is controlled by the reactivity of the adhesive under boiling temperature restraints during the cure.

Dry tensile and boil test results were determined from plywood made using a room temperature setting-nonacid-waterproof adhesive (resorcinol-formaldehyde type) and, subsequently, using a commercial phenol-formaldehyde, exterior grade plywood adhesive (CR-670, pH = 11). In both cases the dry tensile was the same as that using the Holderby formulation. However, the wet tensiles were significantly higher than

the Holderby formulation and the wood failure was predominantly in the wood matrix rather than near the interface as in the latter case. Thus, it appears that the high acid conditions of the Holderby formulation significantly weaken the plywood bond.

Water insolubilities were determined for adhesives of electrodialyzed lignosulfonic acid (ELSA) with resorcinol and paraformaldehyde or phloroglucinol and paraformaldehyde cured by the disk method for comparison with previous data with the ELSA-Catalin system. The variables of phenol-to-formaldehyde ratio (1:1, 1:3), resin concentration (10 to 58% with respect to ELSA solids), pH (1, 2.9, 4.0), time (4, 6 min.) and temperature (275, 345°F.) were examined. The results were about equivalent to the ELSA-Catalin system under comparable conditions. Plywood was made using a ELSA (45%)-resorcinol-paraformaldehyde (1:3) (10%) at 345°F. for 6 min. and dry tensile and boil test results were obtained. These results were equivalent to those obtained using the same formulation with Catalin under the same conditions. Thus, the phenol-formaldehyde components in the formulation are about equivalent to the phenol-formaldehyde resin, Catalin CR-9357.

The CaSSL-Catalin CR-9357 system was tested for water insolubility developed as a function of temperature, time, and concentrations at pH 1, 7, 10, and 12 using the disk method for comparison with previous work. For Resin CR-9357 and its replacement, CR-194, the water insolubility developed was maximum at pH = 1, lower but constant from pH 2.5 to 10 and least at pH = 12. The higher the concentration of CaSSL and the higher the concentration of Catalin the better the water insolubility, as previously observed. The exterior grade plywood adhesive Resin CR-670, was run at pH = 12, and, although the water insolubilities were higher than with the above resins at the same pH, they were still low (44% maximum). These data indicate that the

reactivity of CaSSL with phenol-formaldehyde at neutral to alkaline conditions must be increased if successful plywood bonding is to be achieved.

CaSSL was refluxed at pH = 1 with paraformaldehyde (1%) or resorcinol (3.6%) with the intent of introducing reactive methylol or phenol groups. The water insolubilities of formulations with these pretreated CaSSL and the above resins at pH = 7 and pH = 11 were significantly higher than the corresponding systems with untreated CaSSL. It was of interest to note that simply refluxing CaSSL at pH = 1 gave results equivalent to the paraformaldehyde case.

Plywood made with the paraformaldehyde pretreated CaSSL and CR-194 at pH = 7 failed the boil test. However, when an adhesive joint was made under temperature conditions duplicating the disk method, it passed the boil test. The temperature sensitivity of this adhesive is thus indicated. In addition, the wood failure was essentially in the wood matrix, rather than near the interface, which is additional support for the wood weakening effect of the high acid adhesives and the need to formulate adhesives in the neutral or alkaline state.

Plywood made with the resorcinol pretreated CaSSL and the commercial plywood resin, CR-670, at pH = 11 was only marginally successful in the boil test, primarily due to the adhesive solubility. However, here also the tensile specimens failed primarily in the wood matrix. Although this adhesive is still unacceptable, the pretreatment approach shows enough promise to warrant continued effort.

A brief summary of the project findings is presented. It is concluded that the Holderby adhesive formulation suffers primarily from its high acid content. A future program is then suggested which would improve the adhesive formulation of CaSSL with commercial plywood resin at high pH by a systematic CaSSL pretreatment study.

INTRODUCTION

This is Progress Report Fifteen of Project 2421 entitled: "Investigation of the Relationship Between Lignin Structure and its Mechanical and Adhesional Behavior." The relationship of these properties to lignosulfonate adhesive bonding strength, particularly in plywood operations, has been investigated. The surface tension and viscomechanical behavior of these adhesives were found to be similar to that of phenol-formaldehyde resin, a good plywood adhesive (1-3). The lignosulfonate adhesives suffered from low cohesive strength which can be improved by implementing cross-linking reactions during the adhesive cure (2). The cross-linking effected was evaluated by the degree of water insolubility which was observed to be a direct junction of plywood bond strength (4). The lignosulfonate (pH <1) — Catalin system, which has shown favorable plywood bonding (5), was examined to find the optimum conditions for maximum water insolubility (6). However, the plywood bonding achieved with the best conditions was not acceptable (7).

The measurement of temperature-time profiles of the adhesive in the optimizing studies and in the plywood bonding operation and the influence of these profiles on adhesive performance are reported herein. Experimental evidence of the adverse effect of the low pH adhesives on plywood bonding is presented. The cross-linking reactivity of spent sulfite liquor (SSL) with phenol-formaldehyde systems, including commercial resins, under neutral and alkaline conditions were measured, and methods to improve this reactivity were tested. Plywood bonding studies, as ultimate test of these systems, are presented. Finally, a discussion of the significant findings of the project to date is given, followed by suggestions for future work.

EXPERIMENTAL

MEASUREMENT OF ADHESIVE TEMPERATURE DURING CURE

The temperature of the adhesive region of the glass fiber disk or plywood was measured as a function of time during the hot press adhesive curing process. This was accomplished by placing iron-constantan thermocouples with small diameter (Omega Engineering, Inc., Stamford, Conn., No. 1726275, 0.003 in. diameter, 12 in. leads) at selected points in the region. The head of the thermocouple junction was hammered to a 0.003-in. thickness. These bare wire thermocouples were first insulated with KF-631 (3M Company, St. Paul, Minn.) by dipping in this dispersion, air drying at room temperature for 30 min., and baking at 500°F. for 2 hr. This insulation was not adequate so the thermocouples were then enclosed between Mylar tape, 0.001-in. thick, giving a total thickness of 0.0055 in. This method was successful, so perhaps the KF treatment would not have been necessary.

A thermocouple junction frame to fit the Carver press was built consisting of a 6-3/4 x 8-3/8 x 0.0036 inch copper sheet with two, 10-post terminal strips (Cinch-Jones Type 10-172) attached at each end, accommodating a total of 20 thermocouples. Insulated iron and constantan wires were attached to alternate posts along the terminal strips and were connected to a twenty-position rotary switch (Shellcross Type 4A06A23-1) so that each iron and constantan thermocouple connection was identified with a switch position. Iron and constantan leads then went from the switch to the cold junction (ice water) and a single channel millivolt recorder (Sargent, Model S-72150). The thermocouple EMF was checked with handbook values using water of known temperature for the hot junction.

Although the system was set up for a maximum of 20 thermocouples, only up to 6 were used in a given experimental run. Thus, it was convenient to switch to the various thermocouples by hand and record the temperatures simultaneously with a single channel recorder.

In making a run, the thermocouples were attached to selected terminals with leads sufficient to reach the desired test location. The millivolt recorder was standardized and the cold junction was placed in ice water. The wood veneer and glass fiber disks with adhesive, or the plywood layups were assembled on the copper base of the thermocouple frame, and the thermocouples were placed at the desired points during the assembling. The base with the assemblage then was placed carefully on the lower platen. The press was closed and brought to the desired pressure as quickly as possible. The beginning of the run (about a 10-sec. uncertainty) is then quickly noted on the recorder chart and the thermocouples switched in order every 10 to 20 sec. Each thermocouple is identified on the chart. (The adhesive bubbling from the edges will short the thermocouple if it goes beyond the Mylar enclosure, so this enclosure must extend an inch or so beyond the edge of the veneer.)

DETERMINATION OF ADHESIVE WATER INSOLUBILITY

The cured adhesives were prepared as previously described (4). Three glass fiber filter pads (5.5 cm. in diameter), previously conditioned and weighed, were saturated with the adhesive under study, placed on silicon-treated aluminum foil, backed with a flat brass sheet and 1/8-in. pine veneer, and put in the heated press at 28 p.s.i. for the prescribed temperature and time as described before (8). In some cases, as indicated, the adhesive-saturated disks on the aluminum foil were placed at the inner or outer glue line of a 2-3 ply layup

arrangement of wood veneers. This arrangement more closely duplicates the temperature-time history of the adhesive in the plywood operation. After curing, the disks in the aluminum were again conditioned to 73°F. and 50% R.H. One of them was then removed, weighed and placed in a cotton bag for the boil test.

The bags were then subjected to boiling water extraction for three hours (4). At the end of the boil period, the bags were removed and allowed to dry at 73°F. and 50% R.H. at least overnight. All of the remaining pieces of disk were carefully removed and weighed to constant weight.

The percentage of adhesive insolubility was calculated from the weights of the disk without adhesive, before boil, and after boil.

PLYWOOD LAYUPS AND TESTING

The plywood layups (6 x 6 in.) were made as described previously (3). The adhesive was made up in the same weight ratios of SSL and resin to wood flour as used by Holderby, et al. (5) which is 1:0.36. Using selected southern pine veneer which had been sanded and aged more than two weeks at 73°F. and 50% R.H. (the equilibrium moisture content was 7.4%), exactly four grams of adhesive were applied to each side of the center lamina of a three-ply layup. Two layups were used in each press, except where indicated, and from six to eight layups were made with each adhesive.

Ten 1 x 3-inch specimens were cut and kerfed from each layup as previously described (3). The boil and wet tensile test for exterior-grade plywood (9) was used on every other specimen, and the remaining specimens were tensile tested without boiling. In the boil test, the specimens are boiled in water for four hours, dried overnight at 125°C., reboiled the next day, and tensile measurements were made in the wet state (Amsler Tester was used).

RESULTS AND DISCUSSION

TEMPERATURE-TIME PROFILES

The poor ELSA-Catalin adhesive performance in plywood bonding studies compared to that expected as based on water insolubility measurements of the adhesive in the glass fiber disk studies (6,7) was believed to be due mainly to a difference in the temperature history of the plywood vs. disk systems. In the plywood system two 3-ply layups were cured in one press; thus, there is an inner glue line and an outer glue line. In the disk system, the adhesive saturating the glass fiber-disk was cured between two wood veneers in one press. Temperature-time measurements were made on these systems using the following specific conditions. (Unless otherwise stated, disks mean glass fiber disks, enclosed in aluminum foil, backed top and bottom with a flat brass sheet and a 3/32-inch wood veneer, and a press load of 28 p.s.i.; plywood means two 3-ply layups at a press load of 200 p.s.i. Platen temperatures used are indicated.)

(1) No adhesive; disks: 275, 345°F.
plywood: 275, 300, 325, 345°F. (normal and and 28 p.s.i.)

(2) ELSA (42% solids); disks: 275, 345°F.
plywood: 275, 345°F. (2-ply, 3-ply, two 3-ply, and 28 p.s.i.)

(3) ELSA (45%) — Catalin (5%); disks: 325 (normal and thicker veneer backing), 345°F.
plywood: 325, 345°F.

(4) ELSA (45%) — Catalin (5%) in ethylene glycol; disks: 345°F.
plywood: 345°F.

(5) ELSA (45%) — resorcinol-formaldehyde (1:1) (10%); plywood: 345°F.

(6) ELSA (45%) — resorcinol-formaldehyde (1:3) (10%); disks: 345°F.
plywood: 300, 345°F. (normal and disks in plywood)

(7) ELSA (30%) – Catalin (40%); disks: 300, 345°F.
plywood: 300, 345°F. (normal, 28 p.s.i., and temperature probes in both inner and outer glue lines)

The temperature at random places on the heated platen surfaces was measured and compared with the temperature recorded by the press thermometer located at a corner of the upper platen and used to date in specifying the platen temperature. The measured surface temperatures were about 10° higher than the thermometer temperature in the range of 275 to 345°F. These differences were confirmed by optical pyrometer readings. In addition, there was as much as a 10° variation from point to point along the surface, probably depending on the proximity to the steam heating line. However, the variation was not dependent on position with respect to nearness to center or edge. This was confirmed in glue lines so not many probes were needed in a given glue line.

The data presented in Fig. 1 demonstrate the parameters of greatest influence on the temperature-time plot. (1) The temperature of the disk rises much faster than that in the plywood glue lines, reaching almost full value within 4 min. In the plywood, the temperatures quickly level and rise only slowly after 6 min., the maximum press time used to date, and require up to 30 min. to reach the platen temperature. (2) There is a substantial difference (up to 70°) in the inner glue line and outer glue line of the plywood system. (3) The leveling in the initial temperature rise in plywood occurs at about 220 to 230°F., suggesting that the boiling point of the adhesive is controlling. The outer glue line has at least an inflection at this point and even bare wood veneer shows this, indicating water boiling. (4) The ethylene glycol solvent (a high boiling solvent) adhesive has a significantly slower rate of temperature build-up compared to the water-based adhesives examined (all of these, however,

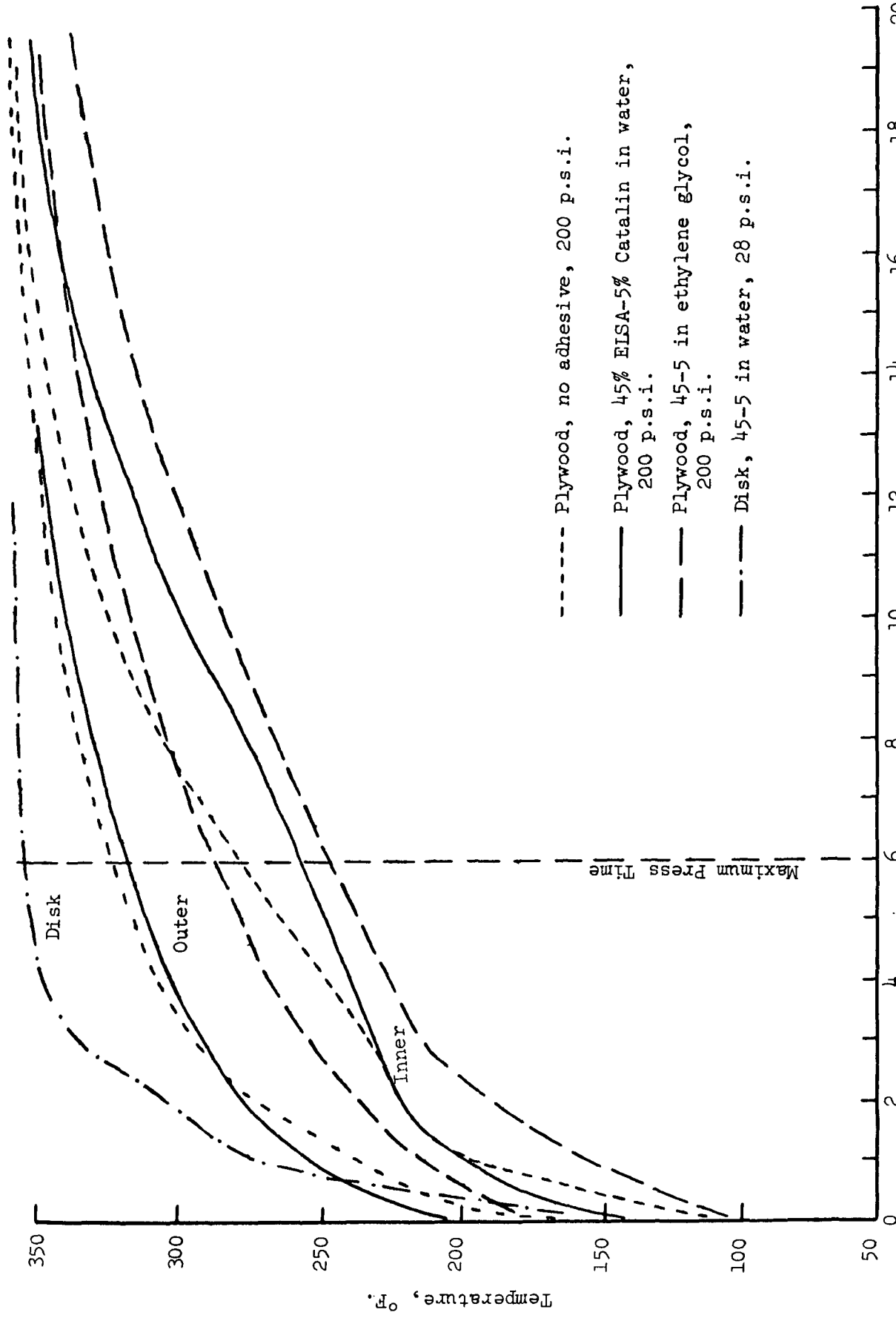

Figure 1. Cure Temperature History with Platen Temperature of 345°F.

have about the same ELSA plus resin solids, 42-46%). It is not clearly evident why this occurs. Perhaps, in water-based adhesives, the process of water evaporation, vapor transportation and subsequent condensation is an important mode of heat transport not available in ethylene glycol systems.

The significant effect of numbers of wood veneers on the temperature-time of a glue line is shown by the data presented in Fig. 2. All of the thermocouples used in these runs are included to indicate the variation of the temperature in a glue line and between glue lines. Again, the single glue line (2-ply) with the heat flux the same from both sides, reaches almost full temperature within 4 min. The temperature variation within the glue line is about 10°, as is observed also in the other systems. The deviation from this 10° variation is believed to be due to the amount of water present at the particular thermocouple location.

The two glue lines in the 3-ply arrangement reach maximum temperature in 9 to 10 min. and they have the same temperature-time profile as expected since each has the same top and bottom heat flux (i.e., two veneers on one side and one on the other). The temperatures are well above the initial leveling point by the time of maximum press. The one thermocouple with quite a faster temperature rise is probably located at a point of low adhesive content.

In the two 3-ply arrangement, the outer glue line (one veneer on one side and five veneers on the other) heats up significantly faster than the inner glue line (two veneers on one side and four veneers on the other) as may be expected due to the dissimilarity of the top and bottom heat fluxes between the two glue lines. Both glue lines are still in the "level" region at the time of maximum press, 6 min., suggesting that the adhesive still has some water content at this

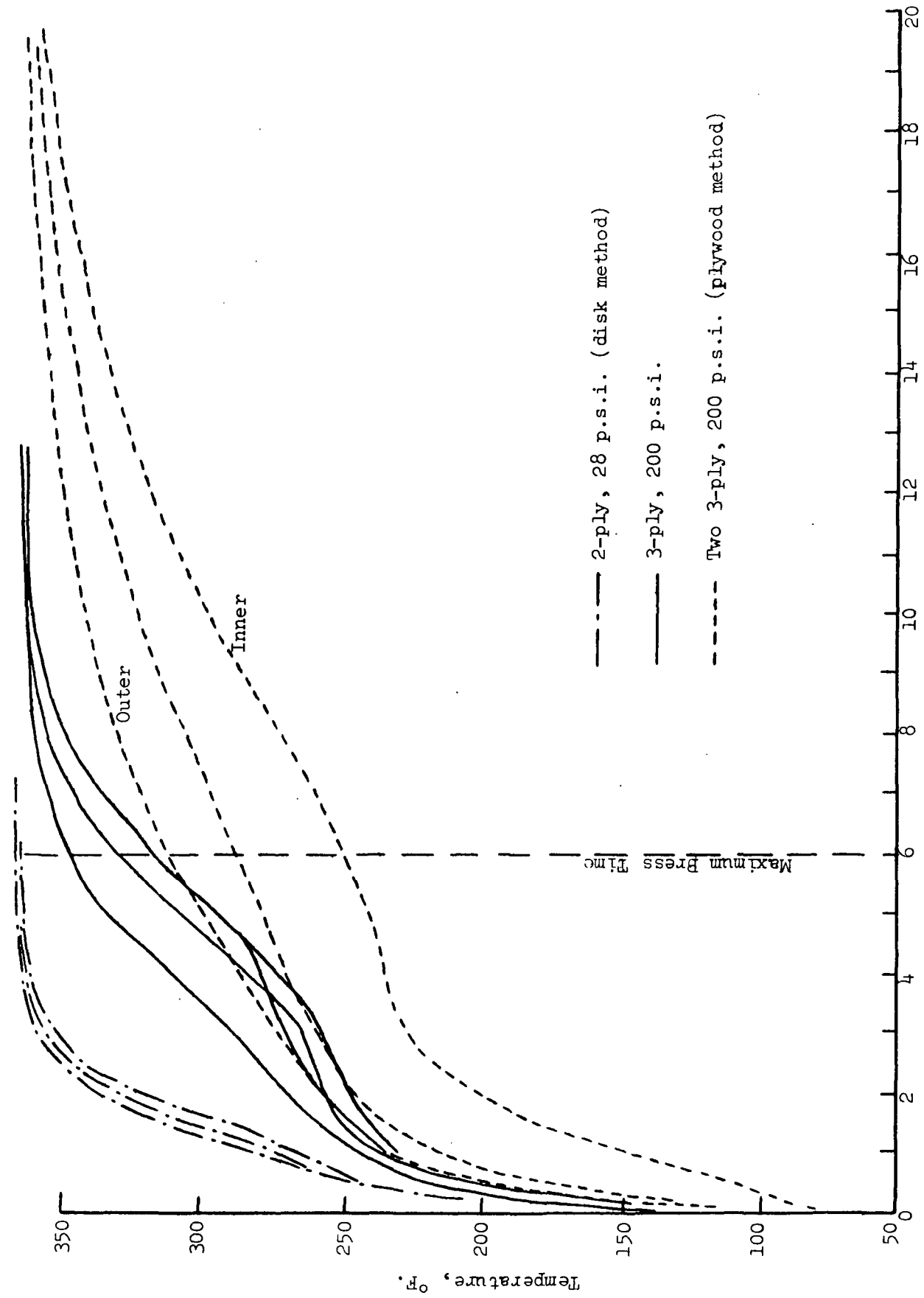

Figure 2. The Effect of Number of Wood Veneers on the Adhesive Temperature; ELSA (42%), Platen Temperature 345°F.

time. It is interesting to note that the initial rapid temperature rise and leveling of the outer glue line is similar to that of the 3-ply system but it stays in the "level" region much longer. This suggests that the initial heating comes primarily through the one-veneer side but that the heat for water removal must flow from both sides. The assumption that the two inner glue lines have the same temperature profile and that the two outer glue lines have the same temperature profile was confirmed by results from a run with a thermocouple in each of the four glue lines.

Although the plywood cure is normally made at 200 p.s.i., it was of interest to see if a lower pressure would affect the profile as the disks had to be run at 28 p.s.i. to prevent them from smearing out to unrecognized forms. The results are presented in Fig. 3. The increase from 28 to 200 p.s.i. causes a slightly faster temperature build-up but the adhesive is still in the level region (i.e., water present) at the maximum press time, 6 min. The increased pressure produces better thermal contact which leads to faster temperature build-up; however, the effect is small.

The effect of different platen temperatures on the temperature profiles in disks is shown by the data presented in Fig. 4. The waves in the 300°F. profile are due to steam pressure variations in the platens causing temperature variations. This pressure is controlled manually by an inlet valve and exit trap and at times the response is quite erratic. Note in each case the maximum temperature reached is about 10° higher than the platen thermometer temperature, which confirms the earlier platen surface temperature data. It is of interest to note that the temperatures almost reached the maximum by the maximum press time, 6 min. Even by 4 min. they are all past the inflection region and well on the way to maximum temperature. However, at the minimum press time of 3 min. they are either in the

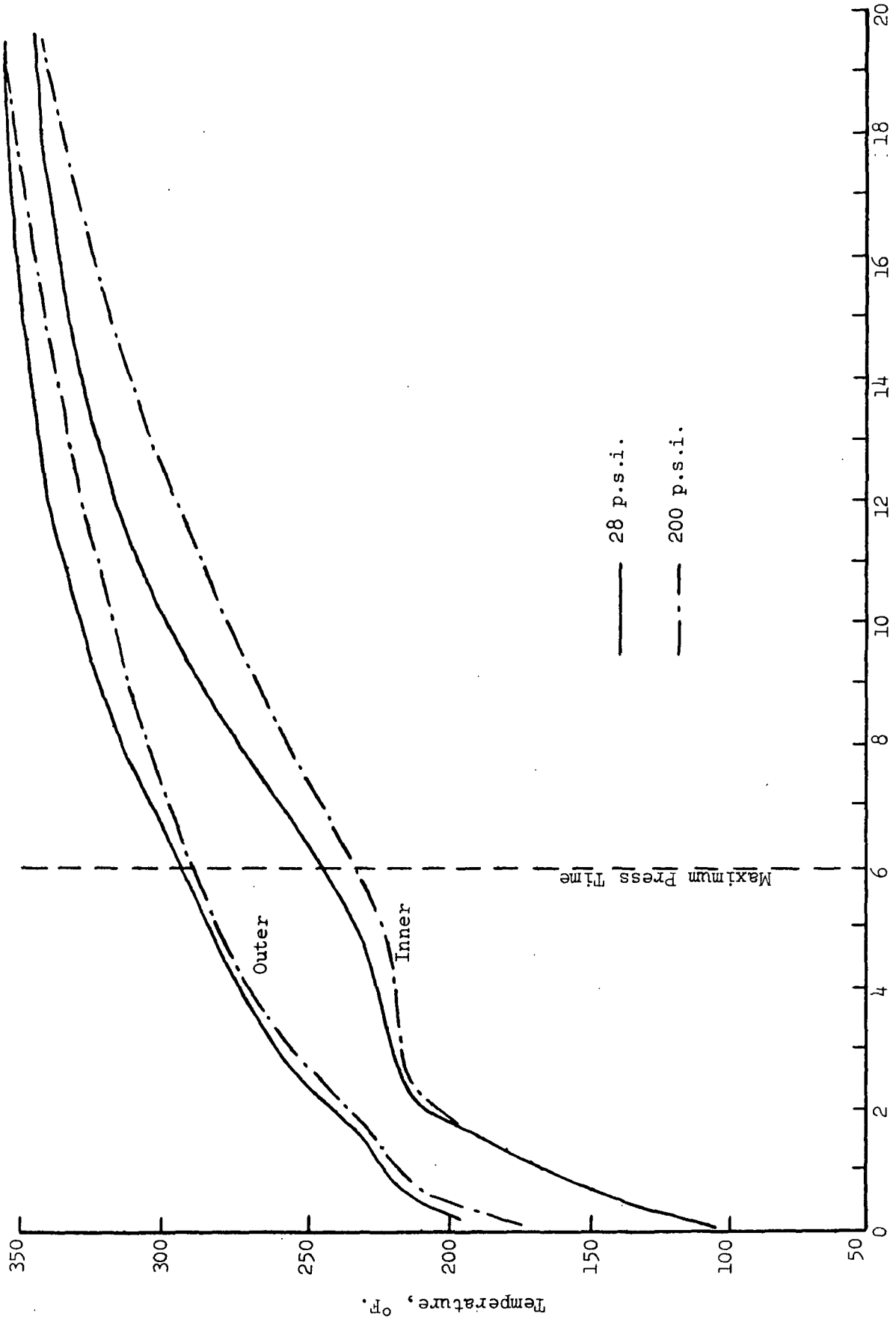

Figure 3. The Effect of Press Load on the Adhesive Temperature; ELSA (30%)-Catalin (40%), Platen Temperature, 345°F.

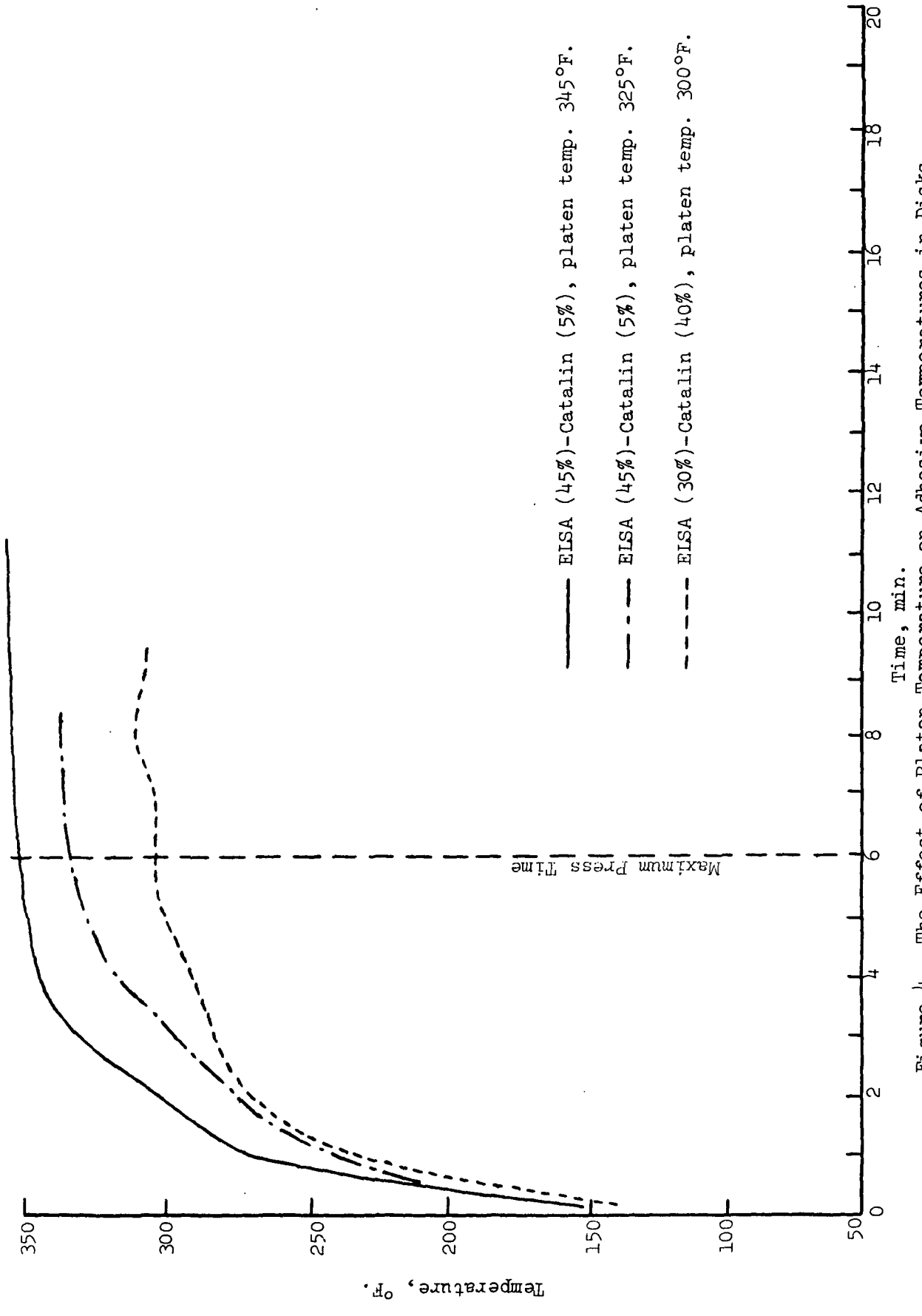

Figure 4. The Effect of Platen Temperature on Adhesive Temperatures in Disks

inflection region (325 and 345°F.) or just entering it (300°F.). It is important to note that there was a significant increase in water insolubility developed between the 3-min. cure and the 4-min. cure compared to subsequent time increases at every temperature tested (6).

The effect of different platen temperatures on the temperature profiles in plywood is shown by the data presented in Fig. 5. The lower platen temperature run takes longer to reach the leveling point, particularly at the inner glue line. By the maximum press time, the higher platen temperature run has gone beyond the level region, indicating that the adhesive temperature is no longer controlled by the boiling process. This point in the lower temperature run is never clearly defined. However, in general, the boiling limitation on temperature causes the temperature profiles at different platen temperatures in the first 6 min. to be similar.

To summarize these results, at a given platen temperature the disk system has a significantly higher temperature than the plywood system at any given time up to the maximum press time, 6 min., and the disk system reaches the platen temperature within this time. In the plywood system there is a significantly higher temperature at the outer glue line compared to the inner glue line up to 6 min. The inner glue line shows a boiling limited temperature within 2 to 4 min. which continues beyond 6 min. for platen temperatures below 345°F., and this boiling limitation makes the temperature profiles for various platen temperatures in the first 6 min. somewhat similar. The ethylene glycol solvent adhesive has a significantly slower temperature build-up compared to the water-based adhesives.

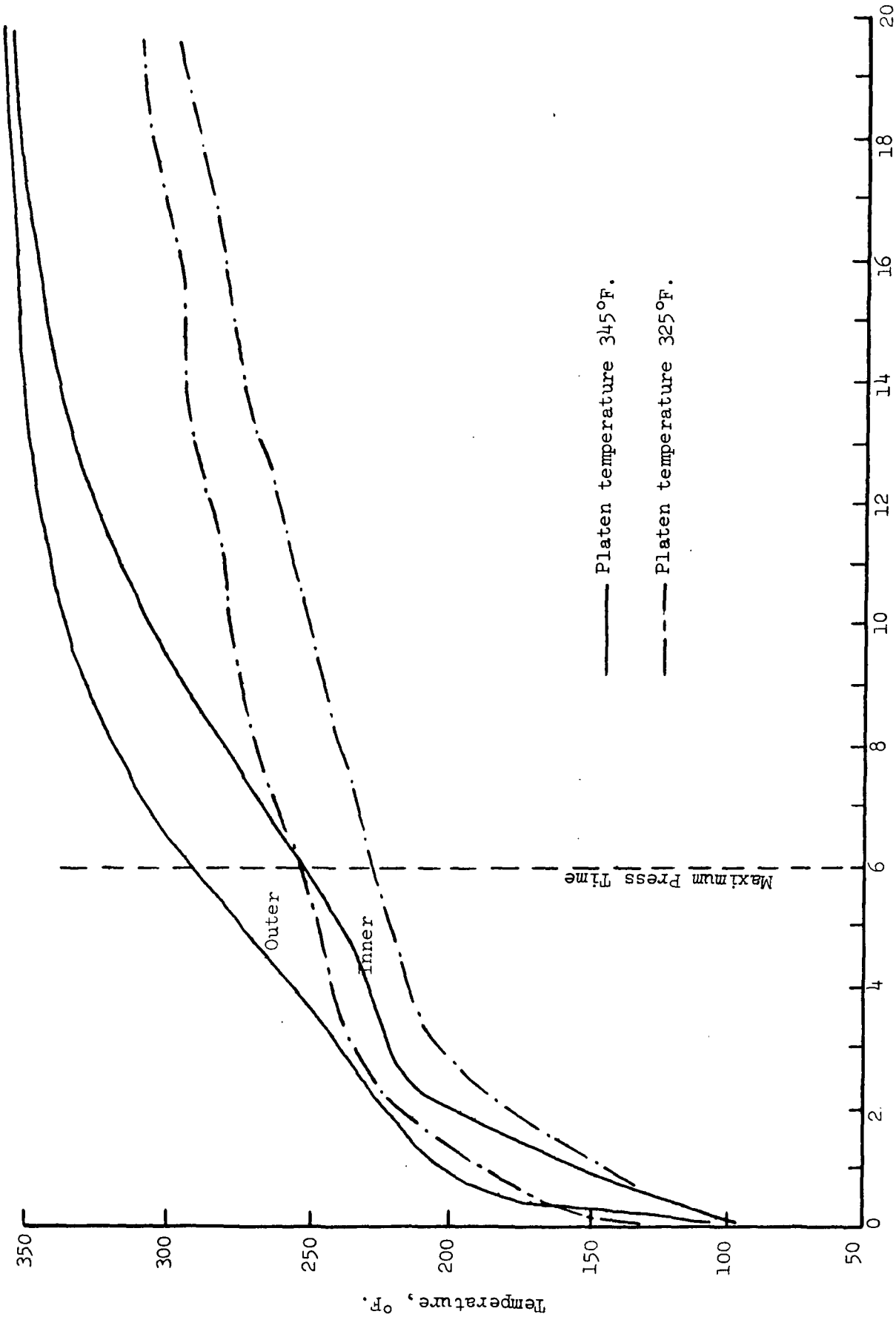

Figure 5. The Effect of Platen Temperature on Adhesive Temperatures in Plywood.
ELSA (45%) – Resorcinol-Formaldehyde (1:3) (10%)

The large temperature-time differences between disks and plywood may account for the lack of success of potentially good adhesives from disk studies in plywood bonding. It would be best to place disks in the normal glue lines in plywood systems for water insolubility studies to achieve correct curing temperature profiles. The relatively low temperatures in the glue lines in the plywood system during the cure time (up to 6 min.) for all the adhesives versus their wide differences in developing acceptable bonding strength, indicates that differences in cross-linking reactivity are of major importance in the performance of the adhesives. These points and the role of adhesive pH were focused upon in the subsequent insolubility and bonding studies.

EFFECT OF DISK TEMPERATURE, INNER AND OUTER GLUE LINE, AND LOW pH ON PLYWOOD BONDING STRENGTH

To observe the effect of the disk temperature profile on plywood bonding for an adhesive which water insolubility measurements suggest as good, the following was done. The adhesive (45% ELSA – 5% Catalin, producing 80% insolubility at 345°F. for 6 min.) was spread (4 g.) between two veneers (i.e., a single glue line) and cured at 200 p.s.i., 345°F. for 6 min., thus duplicating the disk 2-veneer system. After conditioning this 2-ply system overnight at 73°F. and 50% R.H., a third veneer was bonded to it using Elmer's Waterproof glue (Borden Co.), a resorcinol-formaldehyde adhesive, cured at room temperature. This resulting plywood was then tested in the usual way. The results are listed in Table I.

The single glue joint has very good wet survival and a wet tensile as good as that obtained with the standard Holderby formulation [84 ± 20 p.s.i. (7)], although its dry strength is low (Holderby formulation has been about 210 to 260 p.s.i.). The failure zones were similar to those seen in the Holderby sets

showing significant amounts of interfacial wood fiber pulled as well as some wood matrix, usually springwood. Thus, the good plywood bond development and high water insolubility are relatable under equivalent temperature histories. The previous plywood bond failure of this same adhesive is perhaps understandable as the water insolubility data indicated that successful curing of this adhesive was very dependent on temperature (6).

TABLE I

THE PLYWOOD BONDING BEHAVIOR

(Cure Conditions 345°F. for 6 min. at 200 p.s.i.)

		Tensile, p.s.i.		
		ELSA Glue Line	Elmer's Glue Line	Overall
45% ELSA – 5% Catalin (single glue joint)	dry	113 (39)[a]	151 (6)	119 (45)
	wet	74 (48)	54 (1)	73 (49)
		Outer Glue Line	Inner Glue Line	
Elmer's Waterproof glue	dry	--	--	236 (5)
	wet	--	--	195 (5)
42% ELSA – 10% paraform-aldehyde-resorcinol	dry	105 (20)	91 (17)	99 (36)
	wet	21 (10)	23 (5)	22 (14)
		Wet Survival		
		1st Boil	2nd Boil	Overall
45% ELSA – 5% Catalin (single glue joint)		50/50	49/50	49/50
Elmer's Waterproof glue		5/5	5/5	5/5
42% ELSA – 10% paraform-aldehyde-resorcinol		16/40	14/16	14/40

[a] Parentheses designate the number of specimens tested.

Included in Table I are data from plywood bonded with Elmer's Waterproof glue. This is a nonacid, room temperature cured, waterproof glue which eliminates the effects of high acid and high temperature on the adhesive bond. Although only one 6 x 6 plywood board was tested (producing 5 dry and 5 wet tensile specimens), the results were considered significant and were later verified. The dry strength is comparable to that of the Holderby formulation but the wet strength is significantly higher. In addition, the wood failure was entirely within the wood matrix. It appears from these data that the high acid conditions of the SSL adhesives formulated to date lead to a weakening of the wood structure near the adhesive interface. Significant improvements in plywood bonding with lignosulfonates will come only by formulations with pH greater than 1. This point will be considered in depth later.

A set of plywood layups were prepared and specific identification of the outer and inner glue lines was made. The adhesive employed was an ELSA — resorcinol-formaldehyde system, discussed below, which is a promising possible alternate to the Catalin resin (a phenol-formaldehyde resin adhesive). The results are given in Table I. There is no significant difference between the outer and inner glue line. This rather surprising finding reenforces the concept that, under a boiling limiting temperature condition, it is the adhesive reactivity more than temperature, per se, which determines the bonding behavior. When the curing time for these adhesives is continued to temperature equilibrium the insolubilities were comparable to those obtained by the disk method, as shown by the data given in Table II. The insolubility for ELSA (45%) — Catalin (10%) at 345°F. for 6 min. was 89% and for ELSA (45%) — Catalin (5%) it was 83%. Since ethylene glycol is essentially a nonvolatile, water-miscible solvent, the 44% insolubility based on remaining material after cure is equivalent to 80-90%

insolubility based on solids only. When insolubility measurements were attempted on these adhesives in plywood at a cure time of 6 min., the adhesives were too wet for the disks to be handled for quantitative measurements.

TABLE II

THE INSOLUBILITY OF ADHESIVES IN A TWO-LAYUP PLYWOOD PRESS HELD TO CURING TEMPERATURE EQUILIBRIUM

Adhesive[a]	Curing Conditions	Weight of Cured Adhesive, mg.	Insolubility, %
42% ELSA – 10% RF[b] in water	345°F. at 200 p.s.i.	200	83 (inner) 82 (outer)
45% ELSA – 5% Catalin in ethylene glycol[c]	345°F. at 28 p.s.i.	400	44 (average)

[a]The ELSA concentration is given as weight percentage in the original solution and the added solids content is given with respect to the ELSA solids.

[b]Resorcinol-formaldehyde in mole ratio 1:3.

[c]Some water was present from the original freeze-dried ELSA (88% solids) and Catalin (50% solids).

ELSA ADHESIVES WITH VERY REACTIVE PHENOLS AND FORMALDEHYDE

In an effort to increase the adhesive reactivity by replacing the phenol-formaldehyde resin (Catalin) with very reactive component parts, the insolubilization reaction of ELSA (42%) with resorcinol or phloroglucinol and paraformaldehyde was measured. The adhesives were cured by the normal disk method so the results could be compared with those from the ELSA – Catalin system (6). The results are listed in Table III. Paraformaldehyde was used as a low odor formaldehyde source. The insolubilities achieved with phloroglucinol (1:1) and with resorcinol (1:2 or 1:3) were about equivalent to that with Catalin, even though the short gel times suggested higher reactivity. At the high concentrations the gel times were so short that there was not enough

time to make usable specimens. In addition, the phloroglucinol was not all dissolved at the high concentration.

TABLE III

THE INSOLUBILIZATION REACTION OF ELSA (42% SOLIDS[a]) WITH VERY REACTIVE PHENOLS AND PARAFORMALDEHYDE

Conc.,[a] %	Mole Ratio of Phenol to Formaldehyde	Water Insolubility, % 275°F. 4 min.	275°F. 6 min.	345°F. 4 min.	345°F. 6 min.	Gel Time, hr.
40	(1:1) resorcinol	14	36	40	89	24
40	(1:1) phloroglucinol	56	77	70	84	2-1/4
10	(1:1) resorcinol	-15	27	53	69	72
14.3	(1:3) resorcinol	55	54	74	83	2-1/2
48.6	(1:2) resorcinol	67	98	--	--	1-1/2
57.1	(1:3) resorcinol	--	--	--	--	3/4
55.2	(1:3) phloroglucinol	--	--	--	--	1-1/2

[a]The ELSA concentration is given as weight percentage in the original solution and the added solids content is given with respect to the ELSA solids.

The plywood bonding data of an ELSA (42%) — resorcinol-formaldehyde (1:3) (10%) adhesive are given in Table I. The wet and dry tensile and wet survival are about the same as a CaSSL (45%) — Catalin (10%) (pH <1) adhesive [10 p.s.i., 113 p.s.i., and 14/60, respectively (7)], further supporting the equivalence of resorcinol-formaldehyde to Catalin.

The effect of pH on the insolubility reaction of the CaSSL — resorcinol-paraformaldehyde system was studied briefly. The results are given in Table IV. The decrease of insolubility with increase in pH is observed here as with the Catalin system (7). Again, the extent of reaction in the two systems is about

the same. Included in Table IV are some data on insolubilities developed at the inner and outer glue line in a plywood system. No significant difference between the glue lines is discernible. This finding is consistent with the plywood bonding data given above. It is interesting to note that the insolubility developed in the glue lines appears to be higher than that developed in the normal disk method under comparable conditions. This finding is surprising.

TABLE IV

THE pH EFFECT ON THE INSOLUBILIZATION REACTION OF CaSSL (50% SOLIDS[a]) WITH RESORCINOL-FORMALDEHYDE (1:3)

Concn., % [a] Curing Conditions:	Insolubility, %						
					345-6[b]		
	275-4	275-6	345-4	345-6	Inner	Outer	pH
14	-21	11	0	-16	--	--	2.9
49	56	51	38	62	--	--	2.8
57	49	57	56	60	--	--	3.0
14	-7	-5	-9	-31	-36	-55	4.1
49	-3	11	-2	11	43	26	4.1
57	29	39	6	41	37	52	4.1

[a] The CaSSL concentration is given as weight percentage in the original solution and the added solids content is given with respect to the CaSSL solids.

[b] Disks prepared in the two-layup plywood system, with the glue line so indicated.

CaSSL-RESIN SYSTEM AS A FUNCTION OF pH

The phenol-formaldehyde resin has shown the best insolubility reaction with CaSSL at low pH and this type of resin is an excellent exterior-grade plywood adhesive. Therefore, it seems most appropriate to think of the CaSSL-resin adhesive as a less expensive extender of the pure resin adhesive. The need is

then to raise the pH of the formulation to neutral or alkaline conditions while maintaining the insolubility rate achieved at pH $\leq$1.

The reactivity of CaSSL – Catlin (CR-9357) from pH <1 to 4 has been studied previously (7). These studies were extended to include the range of CaSSL concentration, Catalin concentration, time, and temperature previously covered at pH = 1 (6) to pH 7, 10, and 12. To do this, more Catalin resin was obtained from the manufacturer, Ashland Chemical Co., Resin and Plastics Division, Columbus, Ohio. The Catalin CR-9357 was not available but Ashland* CR-194 is the same resin only at higher solids concentration (69% compared to 50% for the latter) so it was obtained. In addition, Ashland* CR-670, a commercial exterior grade plywood adhesive was obtained also.

The results of this extended water insolubility study are presented in Table V, along with comparable data on the new resins. The CR-9357 and CR-194 resins in their as-received state produce nearly complete insolubility even at the lower temperature. The CR-670 produced only moderate insolubility, perhaps because of its low solids concentration (40%). At a given pH, the amount of insolubility increased with increasing time, temperature, CaSSL concentration, and resin concentration. For the most part, only the 30-40 and 45-40 concentrations produced insolubilities greater than 50%. For given conditions of time, temperature, and concentrations, the insolubility decreased from pH 1 condition to pH 7 condition, remained constant from pH 7 to pH 10, and dropped further at pH 12. The data for 30-40, 345°F. and 6 min. were combined with previously obtained data (7) for the same condition and are presented in Fig. 6.

*The names of these resins have recently been changed by the manufacturer:
Ashland CR-194 to Arophene 194W-69, and
Ashland CR-670 to Arophene 670W-40.

The insolubility remains constant from about pH 2.5 to pH 10, increased on the low end, and decreases on the high end.

TABLE V

PERCENTAGE WATER INSOLUBILITY OF CURED CaSSL-RESIN SYSTEMS AS A FUNCTION OF pH

CaSSL-Resin[a]	Resin:	CR-9357 or CR-194 ( )				CR-670
	pH:	1	7	10	12	12
	275°F.-4 min.		88[b] (83)[b]			66[b]
	-6		91 (93)			71
	345-4		92 (95)			81
	-6		94 (93)			75
45-40	275-4		42	47	--	19
	-6		42	54	--	30
	345-4		69	68	37	47
	-6		70	69	42	49
45-20	275-4		--	--	--	--
	-6		--	--	--	--
	345-4		53	18	--	--
	-6		60	15	--	--
45-10	275-4		--	--	--	--
	-6		--	--	--	--
	345-4		--	--	--	--
	-6		--	17	--	--
30-40	275-4	3 (64)	7	--	--	32
	-6	20 (66)	29	27	--	19
	345-4	79 (79)	53	58	13	47
	-6	84 (80)	57	56	35	44
30-20	275-4		--	--	--	-4
	-6		--	--	--	-9
	345-4		34	18	16	-4
	-6		51	25	29	6

[a] The first number is the CaSSL concentration which is given as weight percentage in the original solution. The second number is the added solids content which is given with respect to the CaSSL solids.

[b] Pure resins used as is:
CR-9357 50% solids, pH=8.5
Ashland CR-194 70% solids, pH=7.5
Ashland CR-670 42% solids, pH=10.9.

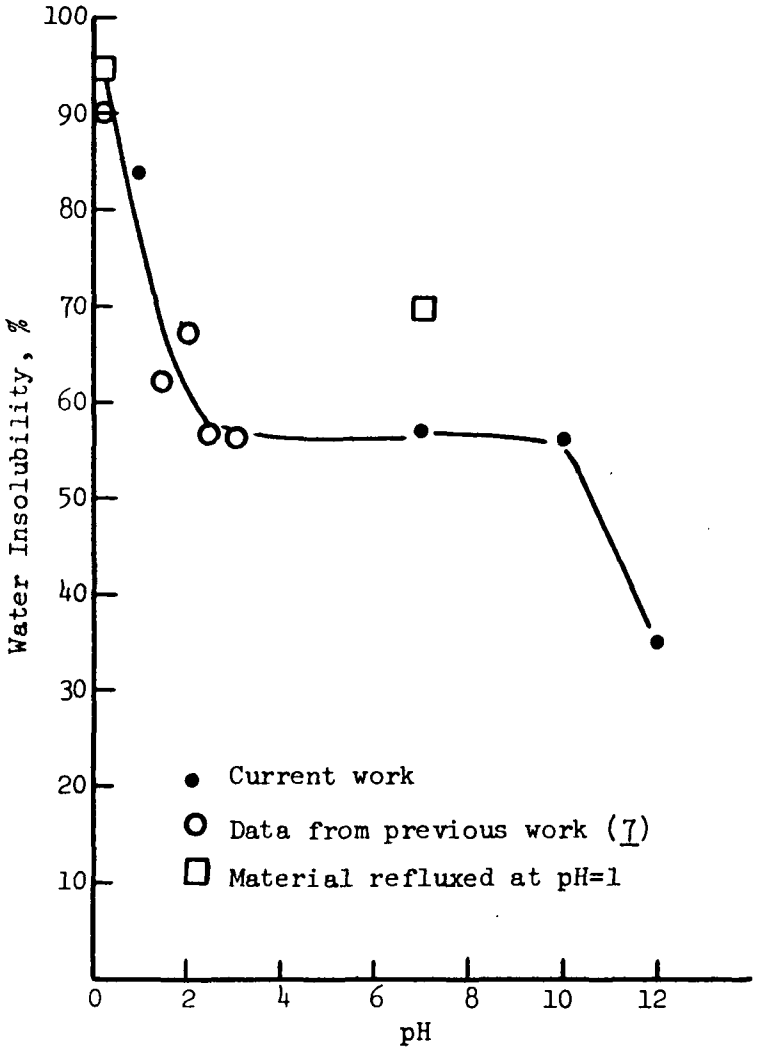

Figure 6. Water Insolubility as a Function of pH for CaSSL (30%)-Catalin (CR-9357) (40%), Disk Method at 345°F. for 6 Min.

The equivalence of CR-194 with CR-9357 is demonstrated by the similarity of water insolubilities for the pure resins and at 30-40 concentrations. The apparent difference at the lower temperature for the latter concentration is an artifact, since previous data (7) on CR-9357 are similar to that obtained for CR-194. The insolubilities with resin CR-670 at pH 12, which is near this resin's normal pH, are disappointingly low. However, in adjusting the pH, local precipitation was observed as drops of strong caustic were added.

CaSSL PRETREATMENT

The insolubility achieved in the reaction of CaSSL with the phenol-formaldehyde at pH >1 and reasonable cure times and temperatures is too low to generate acceptable plywood bonding. It is, therefore, necessary to do something with the CaSSL to improve its reactivity. For reactions with phenol-formaldehyde resins, it would be reasonable to introduce methylol groups to CaSSL via pre-treatment with formaldehyde or to introduce reactive phenolic groups to CaSSL (i.e., novalac) via pretreatment with resorcinol. These pretreatments should be done at pH $\leq$1 because of the high CaSSL reactivity at this pH.

The reaction of CaSSL (50% solids) at pH = 1 with paraformaldehyde at concentrations of 20, 10, 5, 2.5, and 1.0% (with respect to CaSSL) was tried by refluxing for 3 hr. However, all but the lowest concentration produced an insoluble fraction. The only homogeneous material was quite viscous compared to CaSSL at pH = 1 refluxed for the same time. The insolubilities produced by these two samples at pH = 7 with CR-194 and pH = 11 with CR-670 are listed in Table VI. They are about equivalent, which is surprising, and they are significantly better than the untreated sample, which is encouraging. The equivalence suggests that the CaSSL may contain enough free aldehyde (formaldehyde?) to generate methylol groups.

In a similar manner, the CaSSL at pH = 11.7 was refluxed with 20% paraformaldehyde after 3 hr. The material was not much different in appearance or viscosity than CaSSL at pH = 11.7 reflux for the same time. However, as shown by the insolubility data listed in Table VI the insolubility decreased with straight reflux (probably hydrolysis) compared to the untreated sample. The formaldehyde presence brought the sample back to the untreated sample level, which is on the low side.

TABLE VI

PERCENTAGE WATER INSOLUBILITY OF CURED CaSSL-RESIN (30-40)[d] FOR VARIOUS CaSSL PRETREATMENTS

Pretreatment:	None	pH=1 3 hr.[b]	1% Formaldehyde pH=1 3 hr.		pH=11.7 3 hr.	20% Formaldehyde pH=11.7 3 hr.	0.1M Mn[c]		3.6% Resorcinol pH=4.3 3.0 hr.		3.6% Resorcinol pH=1.0 1.5 hr.	3.6% Resorcinol pH=1.0 0.75 hr.	
Disk Location:	Normal	Normal	Normal	Outer Glue Line	Normal	Normal	Normal	Outer Glue Line	Normal	Outer Glue Line	Normal	Normal	Outer Glue Line
pH-1[a] 275-4	3 (64)						(58)	(6)					
-6	20 (66)						(58)	(7)					
345-4	79 (79)						(71)	(52)					
-6	84 (80)						(73)	(74)					
pH=7[a] 275-4	7	(44)	(52)	(--)					(--)	(--)	(46)		
-6	29	(51)	(43)	(--)					(46)	(--)	(49)		
345-4	53	(69)	(69)	(1)					(64)	(16)	(65)		
-6	57	(74)	(72)	(46)					(67)	(58)	(71)		
pH=11[a] 275-4	32		44		-27	30					63	12	22
-6	19		42		12	32					63	20	42
345-4	47		58		22	46					72	35	41
-6	44		65		27	47					73	44	54

[a] Resins used at pH=1 and pH=7 were CR-9357 with no parentheses and CR-194 with parentheses. At pH=11 resin CR-670 was used.

[b] Reflux time.

[c] An amount of $MnCl_2 \cdot 4H_2O$ was added to the 30-40 formulation to make 0.1M with respect to the water content.

[d] The first number is the CaSSL concentration which is given as weight percentage in the original solution. The second number is the added solids content which is given with respect to the CaSSL solids.

There is an indication in cellulose color reversion studies (10) that Mn^{+2} may inhibit acid hydrolysis of cellulose. Therefore, $MnCl_2 \cdot 4H_2O$ was added to the Holderby formulation to see if it would reduce the acid effect on plywood bonding. The effect of this change on the insolubility is shown from the data listed in Table VI. There is, perhaps, a small decrease in water insolubility compared to the untreated formulation but the change should not seriously reduce the wood bonding.

The following attempts to improve the SSL reactivity by the introduction of resorcinol were made:

(1) CaSSL (50%) plus 1% paraformaldehyde was adjusted to pH = 1 with H_2SO_4 and refluxed for 3 hr., then 3.6% resorcinol was added (1:1 resorcinol to formaldehyde ratio) and the reflux was continued for 10 min. Upon cooling, the system solidified.

(2) CaSSL (50%) plus 3.6% resorcinol was adjusted to pH = 1 and refluxed 3 hr., then 1% paraformaldehyde was added. Upon cooling, the system solidified.

(3) CaSSL (50%) plus 1.0% paraformaldehyde was adjusted to pH = 1 and refluxed 3.0 hr. Upon cooling, NaOH was added to bring pH up to 7. At this point the viscosity of the system was much too high to add the resorcinol and reflux as planned.

(4) CaSSL (50%) plus 3.6% resorcinol at pH = 4.3 was refluxed for 3.0 hr. The system was cooled and the pH was adjusted to 7 with NaOH. The water insolubility test was run on this system.

(5) Condition (4) was repeated only the pH was adjusted to 1 and the system was refluxed. Two phases appeared after 1.5 hr. so the reflux was stopped. The system was adjusted to pH = 7

and to pH = 11 and, although the viscosities were very high, water insolubility tests were made.

(6) Condition (5) was repeated only the reflux time was held to 0.75 hr. No two-phase separation was apparent. The viscosity of system when adjusted to pH = 11 was usable for water insolubility and plywood bonding measurements.

The water insolubility on the above usable systems are given in Table VI. When comparing the results for the normal disk method at pH = 7, the resorcinol-treated samples were about as good as the formaldehyde-treated samples. However, the outer glue line results favor the resorcinol treatment. At pH = 11 with CR-670, the resorcinol treatment (No. 5) looks even better than the already favorable (compared to no treatment) formaldehyde treatment. However, the former is two phased and very viscous (like library paste). When reducing the reflux time with the resorcinol treatment (No. 6), the water insolubility drops to about the no-treatment level. However, the outer glue line results look surprisingly good compared to the normal disk data.

In summary, the pretreatments of CaSSL at pH = 1 significantly improved the water insolubility achieved with CR-194 and CR-670 at neutral to alkaline curing conditions. The addition of 0.1M $MnCl_2$ to the pH = 1 formulation did not seriously reduce the water insolubility reaction.

PLYWOOD BONDING STUDIES WITH SELECTED FORMULATIONS

Plywood layups were made to test selected formulations (1) at pH = 1 with Mn^{+2} salt present, (2) at pH = 7 with CR-194, and (3) at pH = 11 with CR-670. The results are listed in Table VII.

TABLE VII

PLYWOOD LAYUPS BASED ON 30-40[d] FORMULATIONS[a] CURED AT 345°F. FOR 6 MIN.

Description	Dry		Wet	
	Tensile, p.s.i.	Survival	Tensile, p.s.i.	Survival
With Ashland CR-194 at pH <1				
Holderby – pH <1	220	40/40	70	38/40
Holderby with 0.1M $MnCl_2$ – pH <1	185	40/40	53	37/40
With Ashland CR-194 at pH=7				
Straight CR-194[a]			--	0/40
CaSSL – pH=1 – 3 hr.			--	0/40
CaSSL – 1% P – pH=1 – 3 hr.			--	0/30
CaSSL – 1% P – pH=1 – 3 hr. – single glue line[b]	238	30/30	80	30/30[c]
CaSSL – 1% P – pH=1 – 3 hr. – double glue line[b]	211	5/5	18	3/5[c]
CaSSL – 1% P – pH=1 – 3 hr. – double layup (repeat)			--	0/10
With Ashland CR-670 at pH=11				
Straight CR-670[a]	295	40/40	145	39/40
CaSSL – 3.6% R – pH=1 – 0.75 hr.	250	30/30	8	13/30
Straight Elmer's Waterproof glue[a]	250	5/5	152	5/5[c]

[a] This includes wood meal in the amount of 0.36 g. for each gram of CaSSL plus resin solids present with the exception of straight Ashland CR-670 where the manufacturer's recommended amount of 0.15 g./g. resin was used and of Elmer's Waterproof glue where none was used. The straight Ashland CR-194 and Ashland CR-670 were diluted with distilled water to give 42% resins solids concentration, which is equivalent to the CaSSL plus resins solids in the 30-40 mixtures.

[b] The single glue line, two-ply system when cooled was made into three-ply using Elmer's Waterproof glue with room temperature cure. The double glue line is one three-ply layup in a press.

[c] The following number of specimens were not tensile tested because of grip failure: 7, 1, and 1, respectively in the order listed.

[d] The first number is the CaSSL concentration which is given as weight percentage in the original solution. The second number is the added solids content which is given with respect to the CaSSL solids.

The presence of Mn^{+2} in the Holderby formulation caused the tensile strength of both the dry and wet specimens to decrease slightly. The Mn^{+2} salt contributes no beneficial effect at low pH.

At pH = 7 the potentially promising pretreated CaSSL systems failed the boil test. Visual examination of the glue line suggested poor water insolubility as the cause. Even the straight CR-194 at the 30-40 equivalent solids concentration failed. It was very low viscosity and perhaps failed more from overpenetration than poor insolubility.

When comparing the outer glue line insolubilities given in Table VI of the refluxed CaSSL (pH=1) with and without paraformaldehyde with the Holderby-with-Mn formulation, it is noted that the latter is significantly better. This suggests that the former two are perhaps quite temperature sensitive in developing insolubility. This possibility is confirmed by the single glue line results of the paraformaldehyde sample. These results are equal to those obtained with the Holderby system, and the double glue line results are intermediate between the single glue line and double layup data. However, the more significant result with the single glue line is that the bond failure was in the wood matrix rather than near the interface. This result is additional support for the weakening effect of the high acid adhesives and the need to formulate adhesives in the neutral or alkaline state. The low wet tensile results compared to the Elmer's Waterproof glue and the CR-670 appear to be due to low water insolubility.

CR-670, a commercial exterior grade phenol-formaldehyde resin, gave excellent tensile, both wet and dry. The bond failure was primarily in the wood matrix, both wet and dry rather than near the interface as in the Holderby case. These results are about equal to those with Elmer's Waterproof glue given here

and previously (7). Although the wet tensile of the bond of CR-670 with the resorcinol pretreated CaSSL is low, it is very encouraging that a modest survival was obtained, indicating that the CaSSL adhesive ability had been significantly improved by the pretreatment. It is unfortunate that perhaps a better choice could have been made for this test as based on the data given in Table VI. However, the results are encouraging enough to justify continued effort on enhancing the insolubility reactivity of SSL as a means of achieving a commercial plywood adhesive.

The surface tension of the CaSSL did not change much with pH (43 dynes/cm. at pH = 1, 46 dynes/cm. at pH 6 to 12, at 73°F.) and the surface tension of CR-670 (61 dynes/cm. at 73°F.) was not much different from CR-9357 (57 dynes/cm. at 73°F.). The wettability of the above adhesive formulations, therefore, did not change much with pH or with resin type used and was not a factor in variations in adhesive bonding.

CONCLUSIONS

The temperature profile in the normal disk method essentially achieves the platen temperature in the press time of 4 to 6 min. used in curing lignosulfonate adhesives. In the two layup plywood system, the temperature profiles of the inner and outer glue lines, although they differ from each, are strongly influenced by the temperature limiting boiling process of the adhesive and of the moisture in the wood. Thus, the glue lines never achieve the platen temperature during the normal cure time.

When the lignosulfonate adhesives are cured under conditions equivalent to the normal disk method, water-resistant bonding is developed as consistent with the water insolubility tests. With the double layup system, the reactivity of the adhesive under boiling temperature restraints during the curing controls the ultimate bonding success. There is no significant difference in the adhesive bond behavior between the inner and outer glue lines.

The SSL is most reactive to phenol-formaldehyde type condensation at pH $\leq$1. However, the wood structure near the adhesive interface is weakened during the curing process by the high acid conditions, placing a serious limitation on the almost acceptable Holderby lignosulfonic acid adhesive. The reactivity of the SSL in the neutral and alkaline conditions can be improved by pretreating the SSL at pH = 1 with formaldehyde or resorcinol. Future work will have to establish the best pretreatment and the quality of plywood bonding achievable under these conditions.

PROJECT 2421 IN SUMMARY

The viscomechanical and surface tension properties of lignosulfonate adhesives were found to be similar to those of phenol-formaldehyde adhesives, indicating good adhesive potential for SSL. The low bonding strength of lignosulfonate adhesives was due in part to their low cohesive strength, providing that the viscosity of the adhesive was sufficiently high to minimize adhesive loss at the wood bonding interface by overpenetration. In order to increase the cohesive strength, methods of implementing cross-linking reactions with the lignosulfonates during adhesive curing were examined using water insolubility of the cured adhesive as a measure of cross-linking. A convenient water insolubility test procedure was established. Improvement of plywood bonding measured by the exterior grade boil test procedure was found when acceptable cross-linking conditions were achieved in the curing process.

Based on a systematic examination of the parameters: spent sulfite liquor concentration, phenol-formaldehyde resin (or its components) concentration, pH, curing temperature and curing time, the following conditions are needed to increase the water insolubility reaction. The limitations in these conditions are indicated also.

(1) Increased temperature — limited by wood charring conditions or equipment design.

(2) Increased time — limited by production rate.

(3) Increased SSL solids concentration — limited by adhesive application when the viscosity becomes too great.

(4) Increased ratio of phenol-formaldehyde resin to SSL — limited by the price of the adhesive.

(5) Decreased pH — limited by wood degradation during the curing process.

The indirect evidence from wet tensile data indicated that the Holderby formulation suffers primarily from number 5, acid degradation of wood. The water insolubility reactivity of SSL under neutral or alkaline conditions must be increased in order to achieve acceptable phenol-formaldehyde type adhesives. Pretreatment of SSL at its most reactive pH (≤ 1) with temperature, time, formaldehyde, and phenol (resorcinol) as variables has produced products with improved reactivity. Such products are potential extenders for exterior-grade plywood, phenol-formaldehyde adhesives.

Through additional effort (see the section on "Suggested Future Program"), it may be possible by this low pH treatment approach to develop single-stage resins or two-stage resins (novolacs), possibly from SSL only. The production of one-stage resins by heating SSL-formaldehyde-phenol-NaOH mixtures has been under much study by others over the year with reported success. Casual experimentation in this area would not be wise.

SUGGESTED FUTURE PROGRAM

Based on the partial success of the pretreatment of SSL at pH = 1, this work should be expanded. The parameters of reflux time and formaldehyde or resorcinol concentration should be surveyed systematically along with the amount of resin needed in the final formulation. The addition of formaldehyde to SSL is the development of a one-stage resin in concept and the addition may possibly be controlled to minimize the amount of commercial resin needed for an acceptable cure. The lower reactivity and higher temperature sensitivity of the SSL system compared to phenol-formaldehyde resins would have the advantages of longer pot life and easier clean up. The addition of resorcinol to SSL is the development of a novolac in concept, requiring a cross-linking component (e.g., paraformaldehyde, hexamine, or a one-stage resin) for cure. Perhaps it would be possible to use it in the dewatered state in fusion reactions. The possibility of replacing resorcinol with phenol in the pretreatment also should be explored.

The necessity of high reaction temperature for curing SSL adhesives suggested that RF heating methods ought to be tested with these adhesives.

The weakest bonding in the wood adhesives is with the summerwood which is more dense and has a higher critical surface energy than springwood. The effect of corona discharge treatment on the bonding of the summerwood should be examined.

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LITERATURE CITED

1. Progress Report Eight, Project 2421, July 22, 1968.

2. Progress Report Ten, Project 2421, July 30, 1969.

3. Progress Report Nine, Project 2421, April 25, 1969.

4. Progress Report Twelve, Project 2421, July 29, 1970.

5. Holderby, J. M., Olson, H. S., and Wegener, W. E., Tappi 50:92A(1967).

6. Progress Report Thirteen, Project 2421, June 8, 1971.

7. Progress Report Fourteen, Project 2421, June 21, 1971.

8. Progress Report Eleven, Project 2421, February 10, 1970.

9. Product Standards Section, National Bureau of Standards, U.S. Product Standard PS 1-66 for Softwood Plywood — Construction and Industrial, Effective Nov. 1, 1966.

10. Czepiel, T. P., Tappi 43:289(1960).

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